Supplemental materials for:

Facile Synthesis of V^{4+} Self-doped, [010] Oriented BiVO$_4$ Nanorods with Highly Efficient Visible Light-induced Photocatalytic Activity

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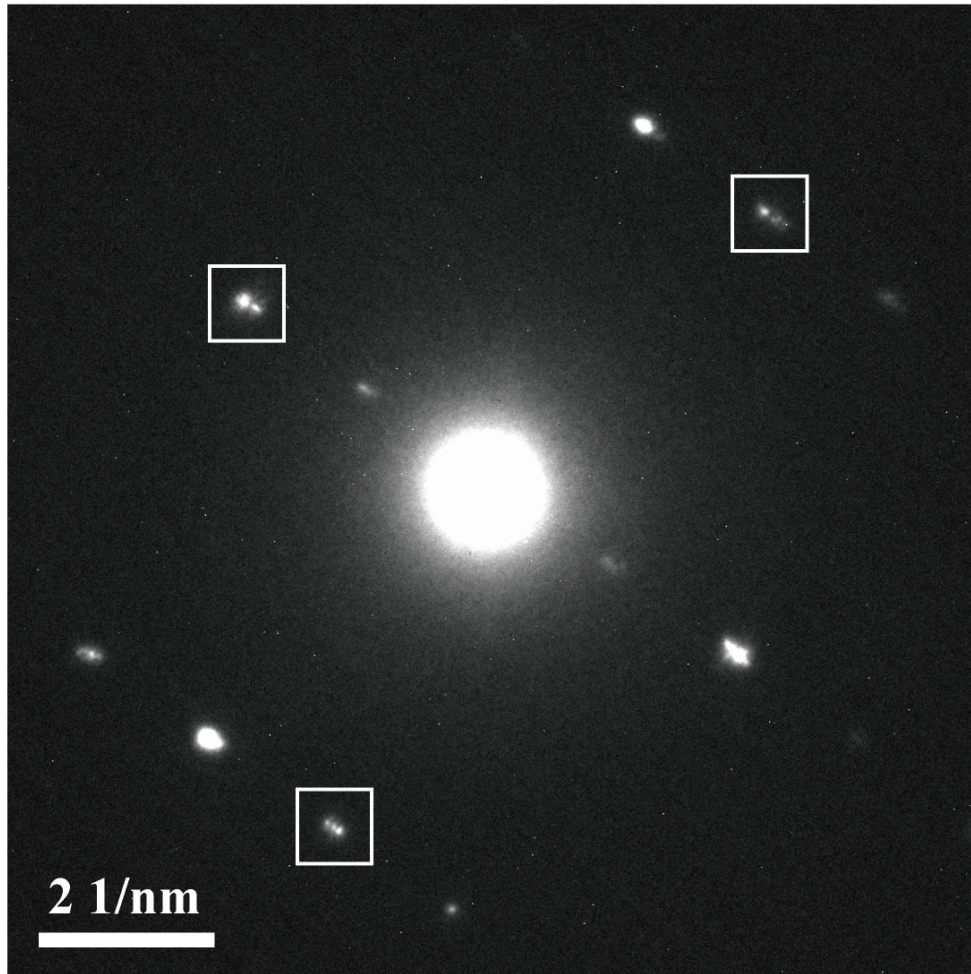**Email Address: ypguo@sjtu.edu.cn (Yiping Guo); hzhliu@sjtu.edu.cn (Hezhou Liu).*

Figure S1. Magnified selected-area electron diffraction (SAED) pattern for the as-obtained BVO-NRs. Obviously, the diffraction spots are a little bit blurry and many of them seem to be made up of two spots, such as the spots circled in white. This phenomenon can be ascribed to the instability of $BiVO_4$ nanorods under high-energy electron beam.
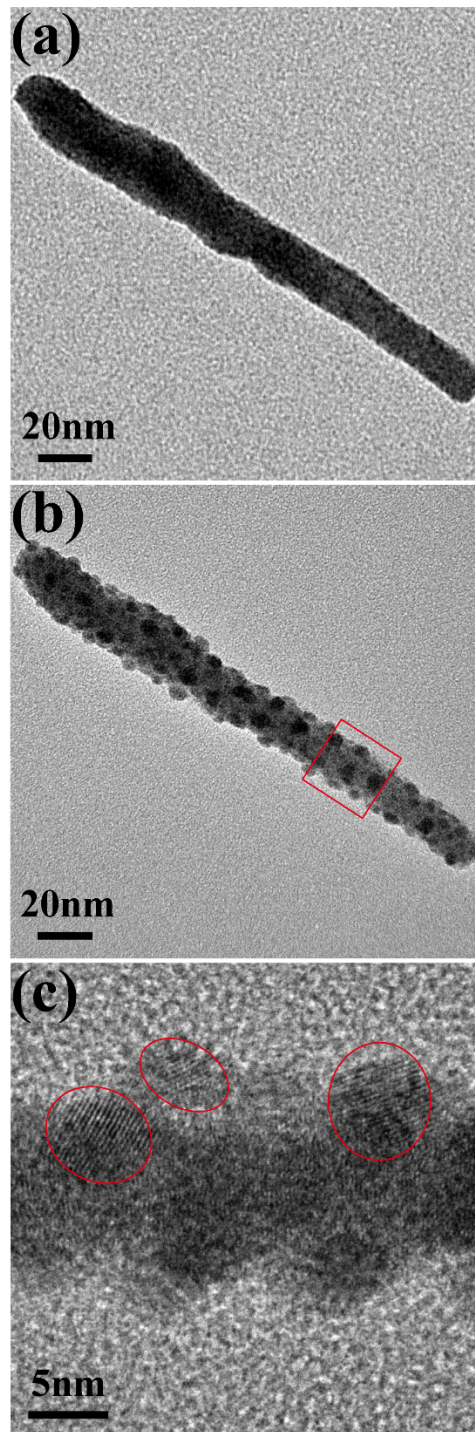
Figure S2. TEM images for one nanorod of BVO-NRs (a) before and (b) after electron beam is focused on, (c) HR-TEM of the destroyed $BiVO_4$ nanorod. After SAED was performed or high-resolution mode was applied for about 5 seconds, the ordered atomic arrangement would be destroyed and $BiVO_4$ quantum dots with dimensions around 5 nm were generated.
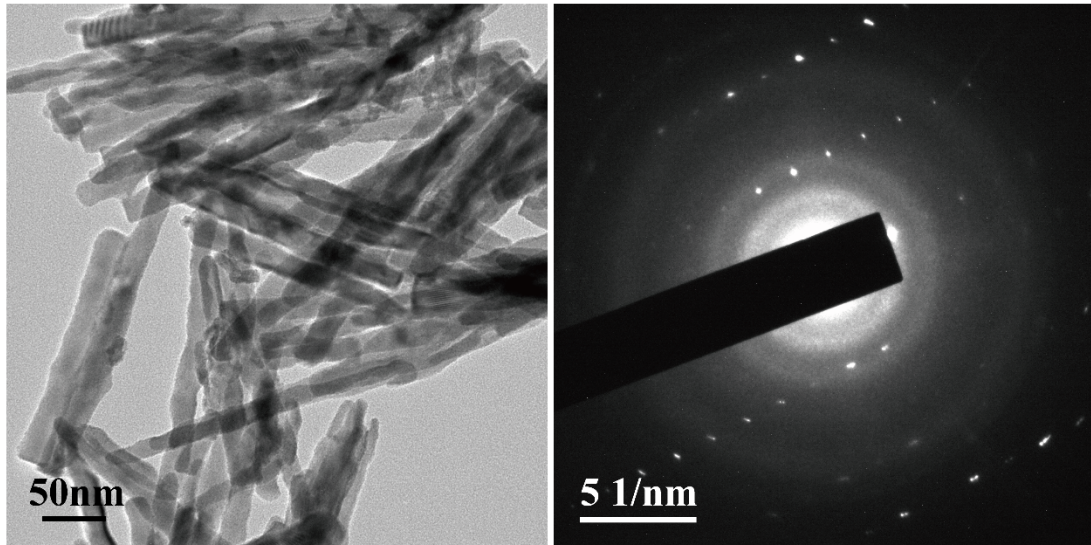
Figure S3. (a) TEM image and (b) SAED pattern for HT-BVO-NRs. Evidently, the morphology of BVO-NRs was well retained after heat treatment at 230 ℃, as well as the SAED pattern.
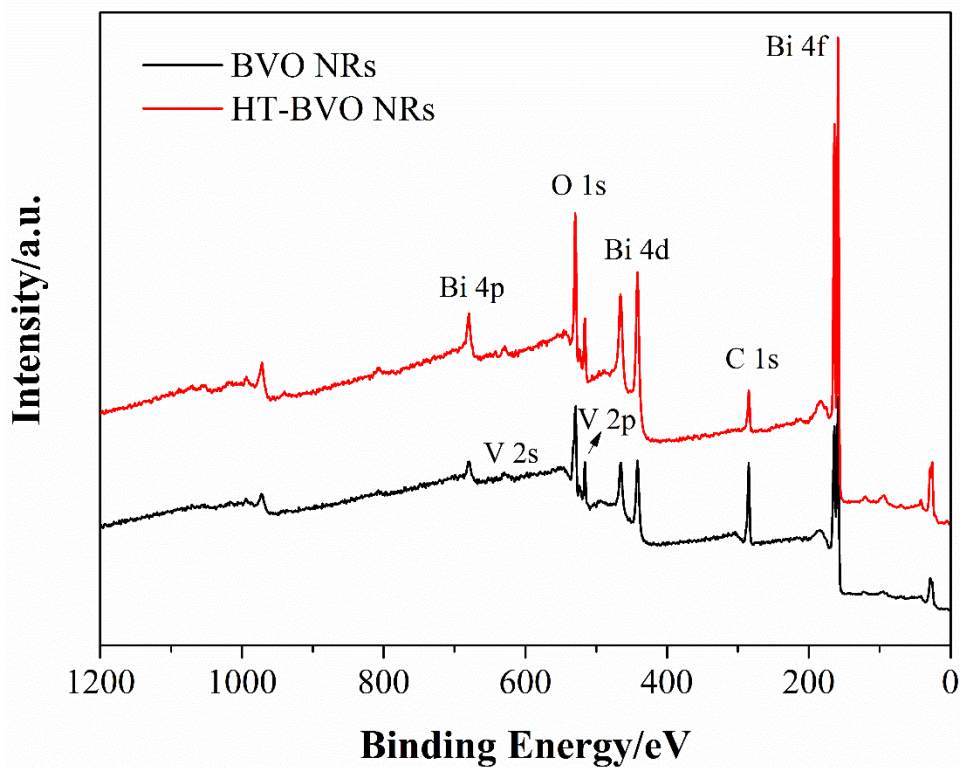
Figure S4. XPS spectra of the BVO-NRs and HT-BVO-NRs.

The broader C 1s peak for BVO-NRs and the small peak at 289 eV for HT-BVO-NRs presented in Fig. 3(a) in this paper should be result from sodium oleate used in the hydrothermal process and its oxidation products. As discussed in the paper, the C=C group in sodium oleate which serves as reducing agent has a probability of being oxidized into H-C=O (aldehyde) and (H)O-C=O (carboxylic acid) groups by broking the C=C group.[1] Similar to sodium oleate, the solubility in water or ethanol of its oxidation products which probably have 9 carbon atoms is not as good as those small polar molecule (i.e. CH_3COOH, CH_3COH). Hence, although the final products (BVO-NRs) were washed for many times with absolute ethanol and deionized water, it was difficult to remove sodium oleate and its oxidation products completely. In addition, the following drying process at 60 ℃ cannot reduce these residual molecule as well due

to their very high boiling point. After heating BVO-NRs at 230 ℃ for 2 h, residual molecules with H-C=O and (H)O-C=O groups are capable of being released owing to high temperature. However, residual sodium oleate (melting point= ~232 ℃) with (Na$^+$)O-C=O group probably keep staying because its chemical properties are similar to salts and 230 ℃ is not high enough to burn it away. As a result, the broad C 1s peak of BVO-NRs should be attributed to the existence of residual reactants with H-C=O (286.0 eV), (Na+)O-C=O (288.8 eV) and (H)O-C=O (289.3 eV) groups while the small C 1s peak of HT-BVO-NRs at ~290 eV should be ascribed to the sodium oleate molecules retained in the sample.

The shift of Bi 4f peaks to higher energy for HT-BVO-NRs should be ascribed to the oxidation some V^{4+} ions. Basically, binding energy values of an element correspond to the attractive force between its nucleus and electrons within different orbits (e.g., 1s, 2s, 2p, etc.). Assuming ion Bi^{3+} and ion V^{5+} are two adjacent ions in BiVO$_4$ crystals, their binding energy will remain unchanged if no valence variation occur. When V^{5+} changes into V^{4+}, the distance between Bi and V is hardly changed because of the restrain of their surrounding ions, however, the ionic radius of V^{4+} becomes larger than that of V^{5+} which leads to a more serious orbits overlap and a higher electron cloud density around Bi. As we all know, the attractive force between the nucleus and its outer electrons will be shielded by its inner electrons, that's why the binding energy of electrons within inner orbits is larger than that of those within outer orbits. 4f is an outer orbit for Bi and will experience an enhanced shielding effect of inner electrons when the electron density around Bi increases. Hence, the binding energy of Bi 4f peak will

decrease as V^{5+} changes to V^{4+} and the verse is also true. As a whole, the binding energy of Bi 4f will shift to higher energy when many V^{4+} species in BVO-NRs changed into V^{5+} species.
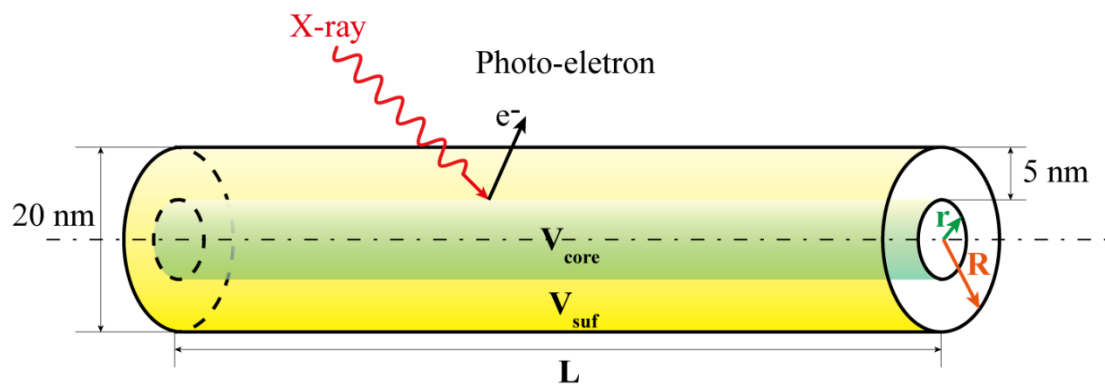
Figure S5. Schematic diagram of a BiVO$_4$ nanorod. The depth that XPS is able to analyze for oxide is around 5 nm. Assuming the diameter of the nanorod was 20 nm. Thus, the proportion of the surface for one BiVO$_4$ nanorod should be:

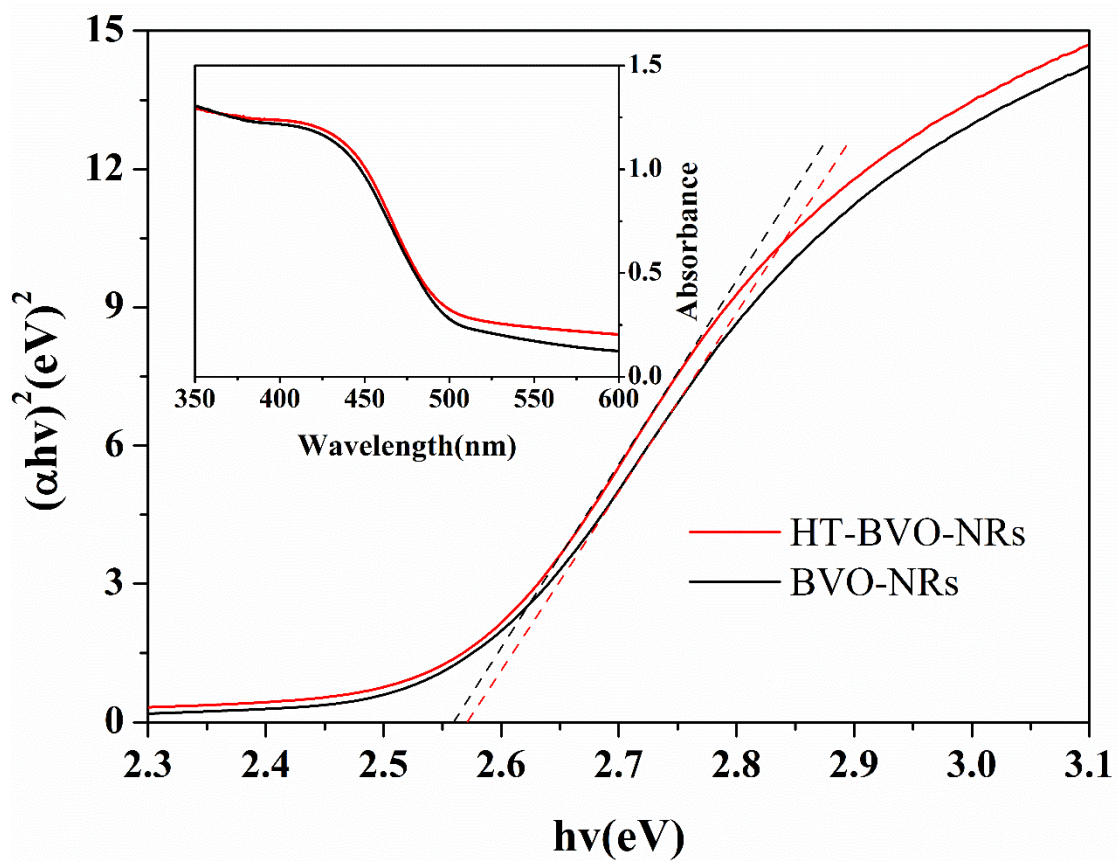$$\frac{V_{suf}}{V_{suf}+V_{core}} = 1 - \frac{L\pi r^2}{L\pi R^2} = 75\%$$

Figure S6. Tauc's plots of BVO-NRs and HT-BVO-NRs, and their UV-Visible absorption spectra are displayed in the inset.
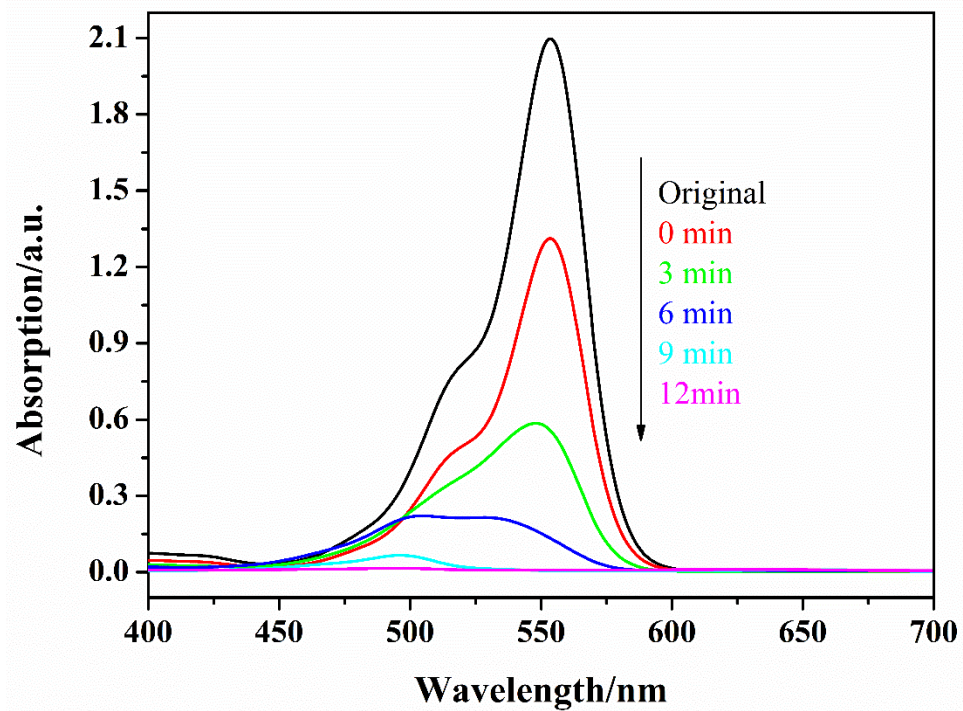
Figure S7. UV-Vis absorption spectra of Rh B aqueous solution at different times using HT-BVO-NRs as the catalyst under visible light irradiation (λ>420 nm).
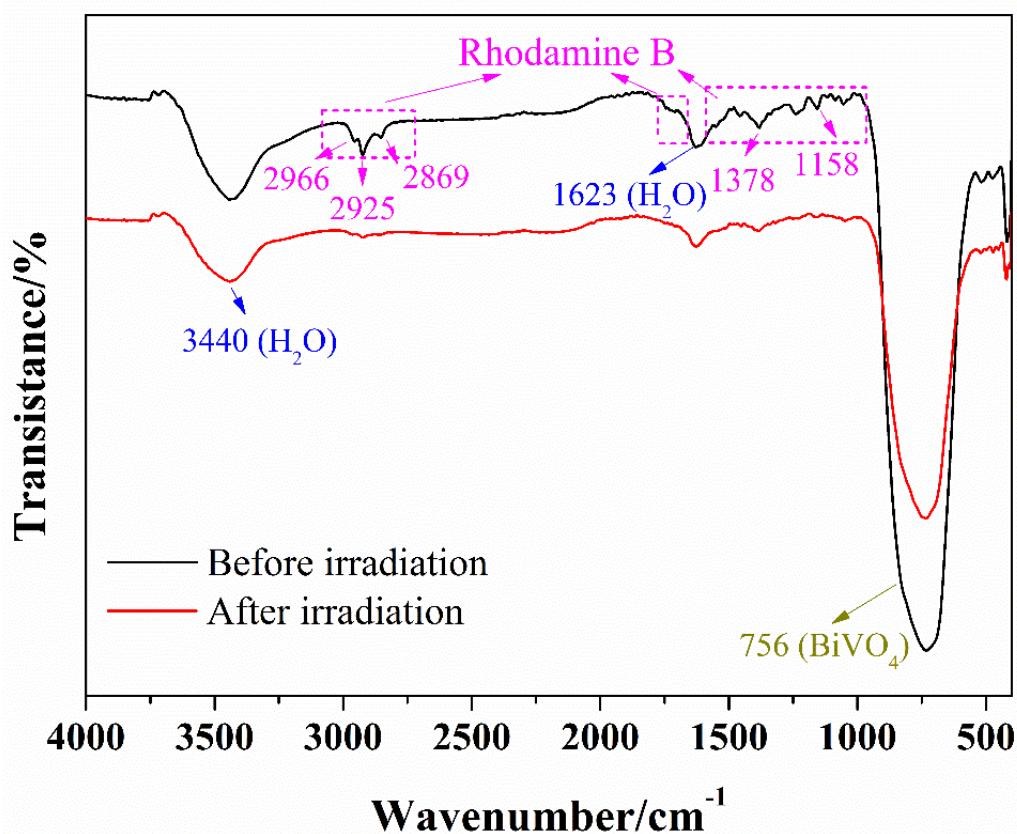
Figure S8. FTIR spectra of HT-BVO-NRs collected before and after irradiation.

The obvious absorptions at 1623 cm^{-1} and 3440 cm^{-1} can be ascribed to bending and stretching vibrations of the adsorbed H_2O molecules, respectively. The strong absorption band at 756 cm^{-1} with a shoulder at 818 cm^{-1} belong to $BiVO_4$. [2] Notably, the absorption peaks at 2966 cm^{-1} (asymmetrical stretching vibration of -CH_3), 2925 cm^{-1} (asymmetrical stretching vibration of -CH_2), 2869 cm^{-1} (symmetrical stretching vibration of -CH_3) belong to Rh B and the circled trivial peaks at lower wave numbers pertain to Rh B as well according to its standard FTIR pattern. [3] It clearly shows that the adsorbed Rh B is also decomposed after photodegradation.
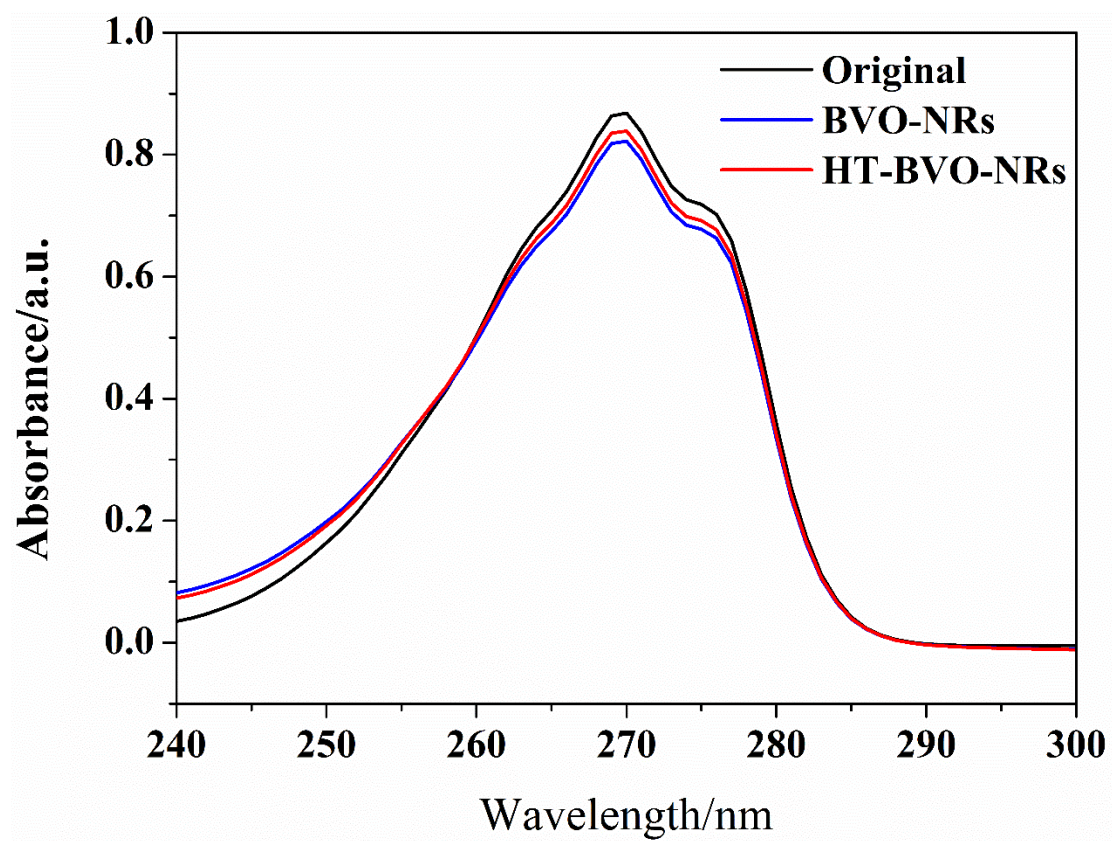
Fig. S9 UV-Vis absorption spectra of (a) 50 mg L-1 phenol aqueous solution, (b) phenol solution after adsorption of BVO-NRs and (c) phenol solution after adsorption of HT-BVO-NRs. Both BVO-NRs and HT-BVO NRs show poor adsorption of phenol.
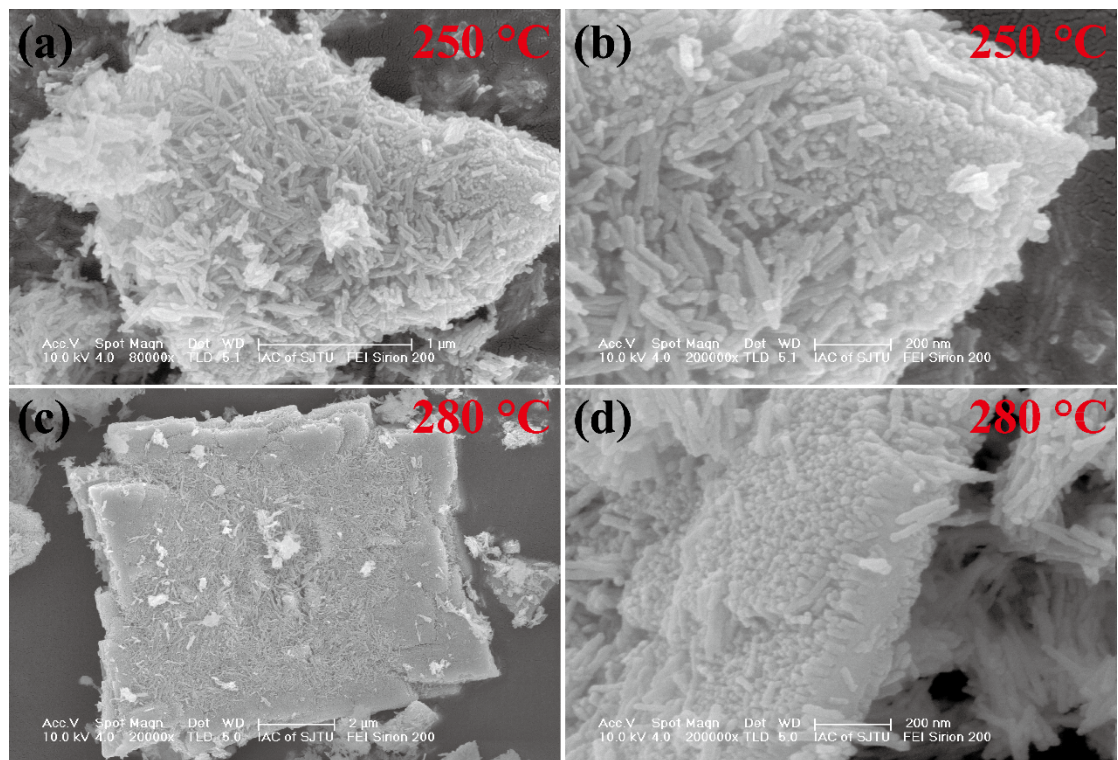
Figure S10. (a) low-magnification, (b) high-magnification SEM images of BiVO$_4$ nanorods heated at 250 ℃ for 2 h, (c) low-magnification, (d) high-magnification SEM images of BiVO$_4$ nanorods heated at 280 ℃ for 2 h.

Name	I_{max}	$I_{15.1°}$	$I_{max}/I_{15.1°}$
m-BiVO4 (JCPDS: 14-0688, I2/a)	100	2.0	50.00
m-BiVO4 (JCPDS: 83-1699, I2/b)	100	3.2	31.25
BVO-NRs	1037	33.0	31.42
HT-BVO-NRs	3277	97.0	33.78

Table S1. The intensities of the strongest peak (I_{max}) and the peak at $I_{15.1°}$ ($I_{15.1°}$), as well as the $I_{max}/I_{15.1°}$ values for BVO-NRs and HT-BVO-NRs are compared in the table. It is well known that monoclinic scheelite $BiVO_4$ (m-$BiVO_4$) has a minor diffraction peak at 15.1° while tetragonal scheelite $BiVO_4$ (t-$BiVO_4$) does not have. Hence, if there is t-$BiVO_4$ coexisting with m-$BiVO_4$, the $I_{max}/I_{15.1°}$ value of the mixture should be larger than that of single-phase m-$BiVO_4$. It can be seen from Table S1 that the $I_{max}/I_{15.1°}$ values of both BVO-NRs and HT-BVO-NRs are either close to or smaller than those of the standard cards, hence, there should be no t-BiVO4 exists in our samples. It is worth noting that the values of $I_{max}/I_{15.1°}$ are different for various standard cards and the two cards we quoted here are just used as reference.

Reference

1 M. B. Smith, *March's advanced organic chemistry: reactions, mechanisms, and structure*, John Wiley & Sons, Hoboken, 2013.

2 D. Ke, T. Peng, L. Ma, P. Cai and K. Dai, *Inorg. Chem.*, 2009, **48**, 4685-4691.

3 http://sdbs.db.aist.go.jp/sdbs/cgi-bin/direct_frame_disp.cgi?sdbsno=15673.